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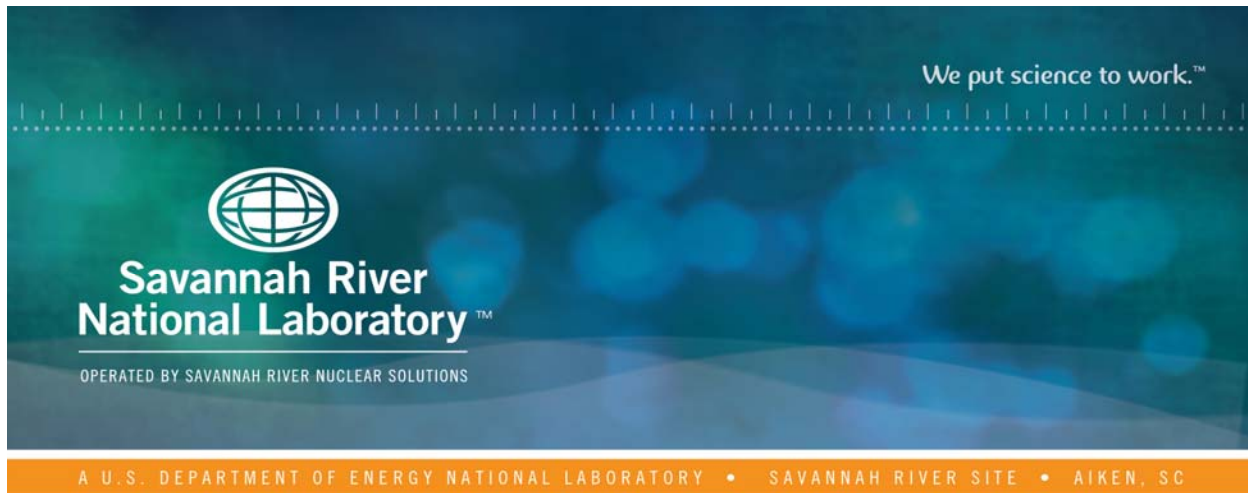
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Overview of Corrosion, Erosion and Synergistic Effects of Erosion and Corrosion in the WTP Pretreatment Facility

K. J. Imrich

March 2015

SRNL-STI-2015-00041, Revision 0



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Printed in the United States of America

**Prepared for
U.S. Department of Energy**

Keywords: *Corrosion*
Erosion
Synergy
Hanford
Waste Treatment Plant

Retention: *Permanent*

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Prepared for the U.S. Department of Energy under contract number DE-AC09-08SR22470.



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EXECUTIVE SUMMARY

Corrosion is an extremely complex process that is affected by numerous factors. Addition of a flowing multi-phase solution further complicates the analysis. The synergistic effects of the multiple corrosive species as well as the flow-induced synergistic effects from erosion and corrosion must be thoroughly evaluated in order to predict material degradation responses. Public domain data can help guide the analysis, but cannot reliably provide the design basis especially when the process is one-of-a-kind, designed for 40 plus years of service, and has no viable means for repair or replacement. Testing in representative simulants and environmental conditions with prototypic components will provide a stronger technical basis for design. This philosophy was exemplified by the Defense Waste Processing Facility (DWPF) at the Savannah River Site and only after 15 plus years of successful operation has it been validated. There have been “hiccups”, some identified during the cold commissioning phase and some during radioactive operations, but they were minor and overcome. In addition, the system is robust enough to tolerate most flowsheet changes and the DWPF design allows minor modifications and replacements – approaches not available with the Hanford Waste Treatment Plant (WTP) “Black Cell” design methodology.

Based on the available data, the synergistic effect between erosion and corrosion is a credible – virtually certain – degradation mechanism and must be considered for the design of the WTP process systems. Testing is recommended due to the number of variables (e.g., material properties, process parameters, and component design) that can affect synergy between erosion and corrosion and because the available literature is of limited applicability for the complex process chemistries anticipated in the WTP. Applicable testing will provide a reasonable and defensible path forward for design of the WTP Black Cell and Hard-to-Reach process equipment. These conclusions are consistent with findings from the various Bechtel National Inc., Independent Review Teams, and Department of Energy (DOE) reviews.

A test methodology is outlined, which should provide a clear, logical road map for the testing that is necessary to provide applicable and defensible data essential to support design calculations.

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LIST OF ABBREVIATIONS

AISI	American Iron and Steel Institute
ASME	American Society of Mechanical Engineers
ASTM	American Society for Testing Materials (now ASTM International)
BC/HTR	Black Cells/Hard-to-Reach
DNFSB	Defense Nuclear Facilities Safety Board
DWPF	Defense Waste Processing Facility
DOE	Department of Energy
E/C	Erosion and Corrosion (synergy)
FAC	Flow-Accelerated Corrosion
HLW	High Level Waste
HTF	Hanford Tank Farm
IGSCC	Intergranular Stress Corrosion Cracking
IRT	Independent Review Teams
LAW	Low Activity Waste
MFT	Melter Feed Tank
MOC	Materials of Construction
NACE	National Association of Corrosion Engineers (now NACE International)
ORP	Office of River Protection
PCDS	Process Corrosion Data Sheets
PJM	Pulse Jet Mixer
PT	Pretreatment Facility
SCC	Stress Corrosion Cracking
SRNL	Savannah River National Laboratory
SME	Slurry Mix Evaporator
SRAT	Sludge Receipt Adjustment Tank
SRS	Savannah River Site
SSR	Slow Strain Rate
WTP	Waste Treatment and Immobilization Plant

1.0 Introduction

This report was requested by the Department of Energy (DOE) - Office of River Protection (ORP) to evaluate the potential for synergistic effects resulting from erosion and corrosion (E/C) of Black Cells and Hard-to-Reach components (BC/HTR) in the Hanford Waste Treatment Plant (WTP) Pretreatment (PT) Facility. Components in the black cells are not accessible and therefore, cannot be replaced or repaired if a failure occurs during their 40 year design life. High Level Waste (HLW) from the Hanford Tank Farm (HTF) will be processed through these piping systems and vessels at velocities ranging from 4 to 12 m/s. The intent of this document is not to give a detailed tutorial on corrosion and erosion, but to demonstrate how corrosion and erosion processes influence each other or “synergy”, which often causes higher than anticipated metal loss rates. It will show how process parameters and design anomalies can result in unanticipated degradation rates. This assessment is based on applicable available literature, including relevant information from the Defense Waste Processing Facility (DWPF), concerning the synergistic effects of corrosion and erosion and how this degradation process relates to piping and vessels in the WTP. In addition, this document presents an outline of a test plan to address the corrosion and E/C issues to provide necessary reasonable assurance the WTP’s materials of construction will perform satisfactorily for their intended design life.

2.0 Corrosion, Erosion, and Erosion-Corrosion

2.1 Corrosion

Corrosion is defined as the degradation (dissolution) of metal resulting from chemical and electrochemical reactions with the environment [1]. The anodic site is where dissolution of the metal into soluble ions takes place, while the cathode is where the electrons are consumed. The two sites can be adjacent to each other on the metal surface, resulting in general corrosion, or some distance apart, which results in localized corrosion. Oxide, and in some cases sulfide or carbonate, films that form on surfaces of metallic materials protect the metal from corrosion. The stability of these layers is critical to protecting many engineering alloys from further corrosive attack. Numerous environmental and material parameters can affect the protective film formation and stability. Some are advantageous while others are detrimental. Factors that will affect film stability include:

- Temperature,
- pH,
- Solution chemistry (inhibitive and aggressive species),
- Agitation (mass transfer and ionic exchange),
- Alloy composition,
- Work hardening,
- Microstructure,
- Grain boundary chemistry,
- Grain boundary area and orientation,
- Inclusions,
- Oxide/base metal lattice parameters,
- Oxide permeation,
- Applied loads (static, residual, cyclic, and thermal), and
- Process changes (wet/dry cycles).

Synergistic effects of the various process chemistry constituents must always be considered to ensure adequate material performance.

The oxide layer that forms on a metal surface protects the metal from further corrosion. This protective layer can either be a thick diffusion barrier like rust on carbon steel or it can be a thin passive film, such as those that form on stainless steels or nickel-based alloys. Insoluble compounds that form by dissolution and re-precipitation are generally not as protective as oxides formed by direct oxidation on the metal surface [2]. The protective nature of oxides formed in dry air was first introduced by Pilling and Bedworth [3]. A similar situation occurs in aqueous environments where there are two types of films that can form with each providing differing degrees of protection. Diffusion barriers are formed by dissolution of the metal and subsequent precipitation on the metal surface [4]. This type of film can also be less dense and contain porosity and tends to be softer and less resistant to damage by an erodent. Passive films are formed by direct oxidation of the metal and are more tenaciously bound to the metal surface. They can also contain porosity or defects depending on the environment in which they form. Adequate physical properties, such as lattice parameter (oxide to base metal) and permeability, and mechanical properties of the protective films are critical to their stability and the ultimate performance of metallic materials in engineering systems [5].

Corrosion can be broken down into two basic categories, general and localized. General corrosion is considered a uniform attack and is relatively easy to predict. Data for general corrosion for metals and alloys can be found in numerous data bases and books such as Handbook of Corrosion Data [6] and NACE Corrosion Data Survey [7]. Data found in these sources provide corrosion rate data for single component systems at specific temperatures and concentrations. These sources do not address complex solutions such as the Hanford HLW that contain multiple aggressive species, inhibitors or localized forms of corrosion. Data can also be found in the public domain in various peer reviewed journals such as those published by the ASM International, American Society of Mechanical Engineers (ASME), and the NACE International. Data taken from any source must be carefully reviewed for quality and applicability. National Codes and Standards such as ASME B31.3 and ASME Boiler and Pressure Vessel Code give guidance concerning corrosion in simple, well understood environments, but caution the designer to use engineering judgment (must be “knowledgeable designer experienced with the Code”) when building systems exposed to complex environments [8]. These National Codes may not be applicable to all or any of the WTP process, but still can be used for guidance. There is an abundance of corrosion data and guidance for single component and very specific environments in the public domain literature, but its applicability to the WTP processes is limited because of the complex HLW chemistry and therefore, must be augmented with testing.

2.2 Localized Corrosion

Localized corrosion is an accelerated attack of a material in a highly confined region. Localized forms of corrosion, including pitting, crevice, galvanic, end grain attack, intergranular stress corrosion cracking (IGSCC), and stress corrosion cracking (SCC), are more complex processes with difficult, if not impossible, to predict degradation rates [9, 10]. For example, the attack (initiation and propagation) rates for pitting and crevice corrosion are not linear because the chemistry inside the pit or crevice will differ from that in the bulk solution (depletion of inhibitors, aggressive species concentration or oxygen concentration cells). Furthermore, as the aspect ratio and geometry of the pit changes or the crevice depth increases, the chemistry may become even more aggressive and form concentration cells that can further accelerate corrosive attack. Flow velocity, which will control mass transfer rates, can affect pit and crevice chemistry. Increasing the flow velocity can have a beneficial effect by increasing flushing of stagnant confined areas, thus minimizing aggressive species concentration, aiding replenishment of inhibitors, and providing aeration. However, if the velocity becomes too high, breakdown of the passive film can occur and result in a potential E/C condition. In the case of IGSCC and SCC, initiation time can vary depending on numerous material and environmental factors such as stress intensity, cyclic loading (thermal or mechanical), microstructure (sensitization), local chemistry, and temperature [11, 12]. These are only a few of the material and process variables that must be considered when designing an engineered system where localized corrosion is anticipated.

Preventing localized corrosion is challenging because there are numerous design features in engineering systems that can exacerbate the problem. Design features that may alter flow rate, create potential differences, or introduce crevices include flanges, unions between dissimilar materials, weld defects (e.g., lack of fusion or penetration), torturous piping configurations, and expanders/reducers. Generally, if there is any potential for localized corrosion mechanisms to affect an engineering system, the prudent solution would be to change to a more corrosion resistant material. In fact, Hastelloy® C-276 was introduced into the test matrix for the DWPF materials of construction (MOC) testing program after pitting and SCC were observed on AISI 304L and 316L stainless steels [13]. Localized corrosion is the most challenging degradation mechanism to control and because its attack rates are so unpredictable, it must be avoided at all cost, particularly in BC/HTR systems that must last forty years. Confirmatory testing for complex environments is the most reliable approach regardless of existing knowledge.

2.3 Erosion

Erosion is defined as progressive loss of material (protective film and/or underlying metal) from a solid surface due to mechanical interaction between that surface and a fluid, multicomponent fluid, or impinging liquid or solid particles [14]. Erosion is also a complex process and can be affected by numerous material and process parameters. As previously discussed for corrosion, the mechanical and physical properties of the metal, oxide and erodent, as well as the process parameters, can affect the erosion rate. The significant metal property affecting erosion rate is hardness, but other factors such as grain boundary area, grain orientation, inclusion content, alloy segregation, and surface finish will also influence erosion. Porosity, hardness, interfacial bonding (chemical or mechanical), and permeability are a few of the oxide film characteristics that will influence erosion. Critical erodent properties are hardness, morphology, friability, mass, and size. Velocity, erodent concentration, and slurry rheology along with angle of impingent are critical process parameters that must be considered when designing for erosion [15]. The WTP history and a discussion of the various parameters affecting erosion were comprehensively discussed by Duignan in 2001 [16].

2.4 Erosion-Corrosion

Corrosion has already been shown to be affected by a number of environmental and material parameters. It can be further influenced by flowing fluids or multi-phase fluids that contain solid particles if they interact with the protective film. Numerous articles and books have been written about this synergistic degradation mechanism concerning numerous metal and alloys exposed to various process chemistries [4, 17]. This review will include literature with a focus on austenitic stainless steels, AISI 304L and 316L since those are the primary MOC for WTP. For clarity, the term degradation in this section will refer to the material loss from both the protective layer and underlying metal surface resulting from the synergistic effect of erosion and corrosion.

Flow-accelerated corrosion (FAC) is a corrosion mechanism that is accelerated by the relative motion of the fluid over the metal surface [18]. As part of this E/C process, the protective film can be degraded by either mechanical forces (e.g., direct particle/fluid impingement) or by flow-enhanced dissolution due to an increase in the mass transfer rate. If the protective film is completely removed or breached locally, corrosion of the underlying metal will occur and may be accelerated. Once the metal substrate is exposed, erosion of the metal may occur if the process fluid or particles have sufficient kinetic energy. A schematic of the effect of fluid velocity on FAC is shown in Figure 1. At a particular velocity the protective layer becomes unstable and degrades quickly. This is referred to as the breakaway velocity. Below this velocity there is a linear increase in the degradation rate, which is attributed to the degradation of the protective film by either erosion or dissolution. Understanding this effect for a particular material

and process chemistry is critical to determining the long-term performance of the material and typically requires testing at representative conditions. In region B (Figure 1), the protective layer is being continuously re-established by diffusion of alloying elements from the near surface region of the underlying metal. In the case of an austenitic stainless steel, these critical alloying elements are chromium and nickel. Over the long-term, the alloy composition in the near surface region will be depleted in chromium and nickel and ultimately become less corrosion resistant. The corrosion rate would increase until reaching a depth where the material had sufficient alloy to repassivate. This cyclic material loss process (E/C to corrosive attack and back to E/C) would be considered quasi-linear. Only if the protective film degradation rate is equal to the repassivation rate will the material loss rate be linear and predictable (see second box from the top in Figure 2). For all other scenarios, the degradation rate will be nonlinear and extremely difficult to predict especially with short-term tests or with tests that lack the complete range of process chemistries. It is unlikely that a linear degradation rate would occur for the anticipated WTP batch-type processing scenario where the process flow is periodically started and stopped.

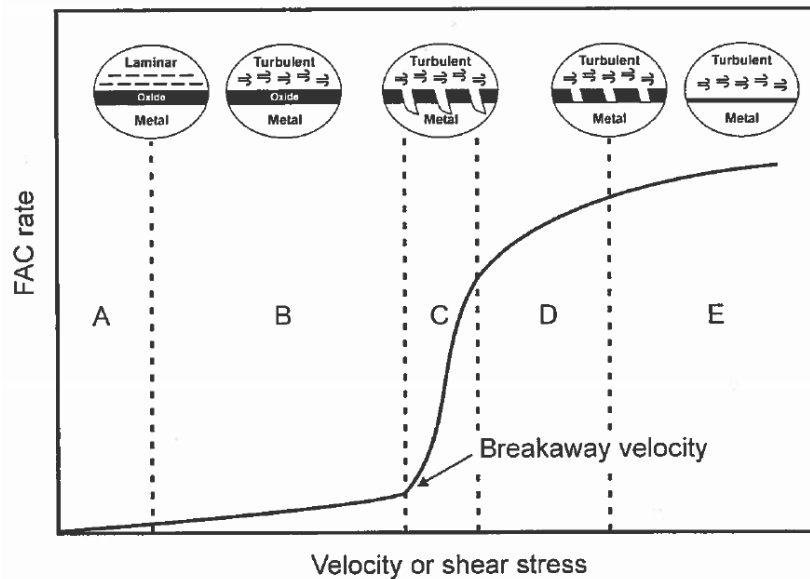


Figure 1. Flow-accelerated corrosion rate versus fluid velocity [18].

Increasing velocity is generally beneficial because it aids in mass transfer, flushing of crevices, and suspension of solids [19]. However, at some point increasing velocity will create turbulence that will result in accelerated attack as shown by the breakaway velocity in Figure 1. Laboratory tests have shown that geometrical irregularities will also create turbulence resulting in accelerated E/C attack [20]. Large mass transfer rate variations were observed behind a machined step in a rotating cylindrical electrode (RCE) test. The data from this test was found to be comparable to that measured in an expansion in a pipe flow loop [21]. This data indicates that repassivation rates in areas where the flow is disrupted would also then be expected to vary from those in the piping systems where laminar flow occurs. Degradation of the protective layer would also be anticipated to vary from region to region in a process piping system due to flow pattern irregularities set up by various design features: e.g., weld defects (such as protrusions or lack of penetration), flanges, orifices, and pipe asymmetry. Buildup of sediment will also disrupt flow patterns. It is this “disturbed” flow condition (vortices) directly adjacent to the pipe wall rather than the bulk flow velocity that must be considered in order to understand E/C degradation [22]. Even under low flow conditions, below the breakaway velocity, buildup of sediments can disturb laminar flow conditions and result in turbulence (sweeps and bursts) with increased impact velocities and

impingement angle shifts that would be conducive to damaging the protective layer [23]. If the protective layer is compromised in discrete locations, the base metal can become at risk for localized attack (pitting, SCC or IGSCC). Localized attack should be avoided because it can accelerate and result in catastrophic failures. If localized attack is suspected, the following options should be considered:

- Control the process chemistry to avoid the problematic environmental condition,
- Modify the system design, or
- Select a more corrosion resistant material.

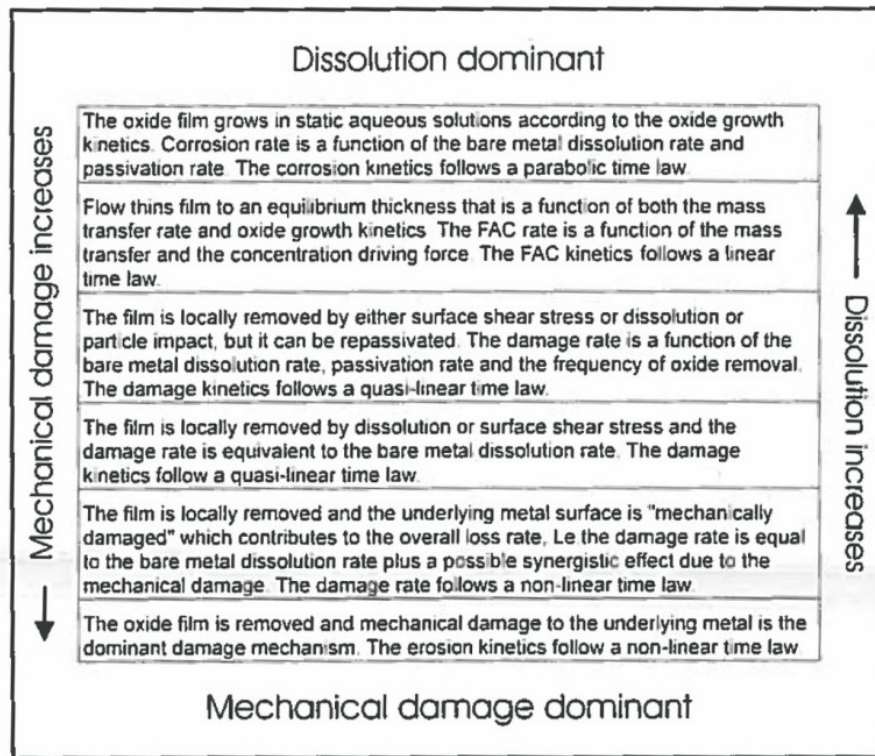


Figure 2. Types of degradation and rates in flowing fluids [18].

Disruptions in the boundary layer in turbulent flow conditions will create even higher velocity sweeps and bursts. These are complex flow patterns that can form under specific conditions which can dramatically affect E/C and the degradation rates. The sweeps and bursts had been postulated and the particle velocities were estimated in these localized turbulent regions. In 1978, the three-dimensional aspects of these flow patterns and their interaction with the pipe wall were actually filmed [23]. Figure 3 shows schematically how they form. The degradation will be amplified with multi-phase solutions such as those with entrained solid particles. If the kinetic energy of the particle is sufficient, work hardening of austenitic alloys such as 304L and 316L will result and transform some of the austenite to martensite. The martensitic phase is not as corrosion resistant as the austenitic phase, so preferential dissolution of the martensite would be expected in the presence of a corrosive media. Wood demonstrated that small near-surface microstructural changes resulting from particle impacts would influence the E/C rate of 316 stainless steel [24]. The testing was performed in a slurry pot at 7 m/s in a solution containing 3.5 percent NaCl with 1 percent silica. Although work hardening resulting from interactions with the slurry in the WTP 316L is piping unlikely, that is not the case for the wear plates below the pulse jet mixers (PJM's) or other portions of the system where flow velocities are increased. The increased kinetic energy of the particles due to velocity may result in work hardening of the wear plates. Therefore, testing of this

potential E/C condition using a full simulant (i.e., chemistry and solids) would be required to evaluate the degradation rate of the wear plates. In addition, work hardening resulting from various fabrication processes (cold bending, heavy grinding, etc.), which could potentially transform some of the austenite to martensite, can also make the stainless steel more susceptible to corrosion and E/C degradation.

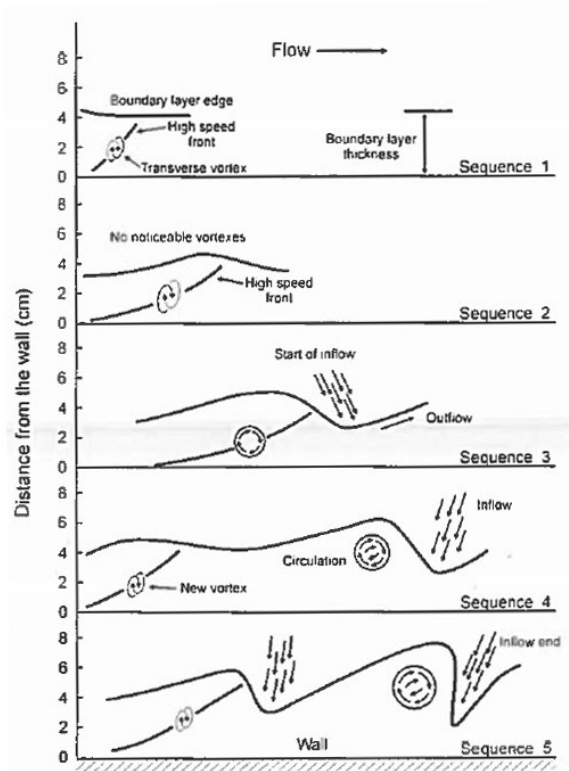


Figure 3. Schematic representation of sweep and burst formation [23].

Numerous tests have been developed to evaluate the complex interaction of material and environmental conditions that occur in E/C. The American Society for Testing Materials, now known as ASTM International, (ASTM) has issued guides for determining synergism between erosion and corrosion and for selecting erosion tests [25, 26]. The tests recommended by ASTM have been reviewed by subject matter experts and proven to provide reliable data. However, these tests do not cover all applications. Ultimately, the test that is selected should model the actual system. Examples of tests that could be adapted are the Georgia Iron Works Coriolis and the rotating cylindrical electrode tests [27, 28]. Other potential E/C tests are described by Roberge [29]. Because of the complexity of the WTP process chemistries and the system “Black Cell” design, confirmatory MOC testing is the most reliable approach to ensure the 40 year service life of the WTP.

2.5 Evaluating Corrosion and Erosion-Corrosion for the DWPF

2.5.1 Initial Corrosion Testing for the DWPF

The following paragraphs describe some of the MOC related challenges that were encountered in the various phases of testing, design and operation of the DWPF. Although the DWPF and WTP systems are ultimately designed to stabilize high-level waste, all the processes and components and MOC are not a

one-to-one match, and therefore, experienced, knowledgeable materials engineers should use caution when applying data from DWPF to WTP.

DWPF was a first of a kind facility in the United States and was designed to process highly radioactive waste that contained many aggressive anions through a large pH range (13 to 3) at elevated temperatures. Corrosion testing for the DWPF began in 1981. Based on years of Canyon processing history at SRS, it was thought that AISI 304L and AISI 316L would be candidate materials for the newly conceived DWPF process. However, during the initial corrosion screening tests, these austenitic stainless steels were shown to experience pitting attack at 50 °C and when the temperature was elevated further, SCC became evident. Both materials were eliminated from further testing leaving just alloy 20CB-3 and C-276 [13]. In another test, evaluating the effects of trace amounts of mercury (0.45wt% Hg as 50% Hg₂Cl₂ and 50% HgCl₂) in an off-gas condensate tank solution, Alloy 20CB-3 was found to experience a 0.2 inch/yr corrosion rate. Other corrosion resistant alloys experienced unacceptable corrosion rates in this mercury containing solution and were also eliminated from the test matrix leaving only C276 as an acceptable material [30]. Thus, after testing in full simulants, many of the seemingly acceptable alloys were excluded as candidate DWPF MOC.

2.5.2 Testing Strategy for the DWPF

Numerous laboratory bench-top tests were to be performed in support of the various DWPF processes. Because of the complex SRS HLW chemistry and the varied processing steps in the DWPF, the Savannah River Laboratory recommended testing be performed using simulants with chemical and physical properties comparable to that of the SRS waste. In addition, large-scale tests, even full-scale when necessary, using these simulants were also recommended in order to fully understand material and component behaviors under prototypic DWPF processing conditions. Some of this testing was performed in parallel with the DWPF construction and required close coordination of the design authority with the design agency. Even with all the laboratory and scale tests that had been performed, it was recognized that they did not adequately represent the actual DWPF processes and system (test duration, full scale components in the exact system configuration, etc.). Therefore, it was decided that material and component evaluations would be performed during DWPF cold commissioning. To monitor corrosion and E/C during cold commissioning, coupons were installed in anticipated trouble spots that had been identified by previous tests. At the completion of cold commissioning, the coupons and critical DWPF components were inspected and documented in the DWPF Materials Evaluation Summary Report [31].

2.5.3 Large-scale testing for the DWPF Feed Preparation System

The feed preparation portion of the DWPF contains three major processing vessels, the Slurry Receipt and Adjustment Tank (SRAT), Slurry Mix Evaporator (SME), and Melter Feed Tank (MFT). The SRAT is a heated vessel that is used to pH adjust the HLW feed. Corrosion and flow corrosion are the primary materials challenges in this vessel. Minor chemistry adjustments are made in the SME along with the addition of the abrasive borosilicate frit. Corrosion and E/C are significant issues in the SME as the multiphase solution is refluxed to approximately 40 wt% solids. The MFT is a holding tank and therefore, no chemistry modifications are made while the waste is in this vessel. Erosion and corrosion were of some concern in this vessel, but particle velocities are lower than in the SME because the viscosity is higher.

Evidence of E/C was first observed in tests containing glass frit in early 1981 austenitic stainless steels. As testing proceeded, pump failures associated with E/C were observed. Many other questions arose during this early test phase for the DWPF, which centered on the rheological properties and pumping characteristics of simulated sludge and simulated sludge with frit. In order to evaluate different pump

designs, and to evaluate the E/C response of full-scale equipment and piping systems, prototypic flow loops were constructed and operated at SRS and at off-site facilities [32, 33, 34]. These tests showed the following:

- Unformanated sludge and formanated sludge (i.e., untreated and treated with formic acid) behaved like Bingham plastic fluids,
- Settling of the simulated slurries was not observed,
- Erosion rate in straight piping was < 0.01 inch/yr at fluid velocities < 8 ft/s (2.4 m/s), and
- E/C rate for flat agitator blades was < 0.3 inch/yr.

A full-scale dual use Hastelloy C-276 (C276) processing vessel, prototypic of the DWPF SRAT and the SME vessels was used for flowsheet mixing and E/C testing. Figure 4 shows a schematic of the DWPF vessel, coils and agitator assembly. During testing with a prototypical DWPF simulant, at a prototypic agitator tip speed of 10 ft/s (3 m/s), severe erosion of the C276 agitator blades was observed. To mitigate E/C degradation, significant design changes were made to both the upper hydrofoil and lower flat blades, which included the introduction of fully welded C276 blades. The timing of the testing allowed the modified agitator assembly to be placed into DWPF service prior to cold (non-radioactive) operations. Agitators incorporating the new design were installed in all three DWPF feed preparation processing vessels: SRAT, SME and MFT.

Following DWPF's 1994 eighteen month cold commissioning, inspections were performed on all systems in the DWPF facility including the feed preparation, melter, and melter off-gas system components. Corrosion coupons that had been placed throughout the facility prior to cold runs were also removed for inspection at this time. Visual inspection of the agitators from the SRAT, SME, and MFT revealed evidence of significant degradation only on the SME agitator. Degradation was most severe on the back sides where the blades were welded to the hub (Figure 5). The degradation was associated with vortices that formed as the slurry flowed around the blade and interacted with this step. The initiation of a similar wear pattern was observed on the agitator blades removed from the full-scale SRAT/SME vessel, but because run times were short, the full extent of the E/C degradation was not revealed and was considered to be acceptable. An important point to note is the performance difference between the agitators in the SME and the SRAT. The lack of significant degradation on the SRAT agitator illustrates that flow corrosion was minimal and that an erosion or possibly an E/C condition existed in the SME as a result of the frit blending process. The degradation was not observed in the MFT probably because the particle velocity in the viscous slurry was significantly lower than that in the SME cycle.

As the facility began radioactive operations in 1996, critical locations on the blades were hard-faced with Stellite and the agitator assemblies were installed. Erosion problems still plagued the hard-faced SME agitator blades. Coil failures in locations adjacent to the vertical coils supports began to occur during radioactive operations. The failures were attributed to vortices created by the rectangular solid bar supports and the flow of melter feed through the coils.

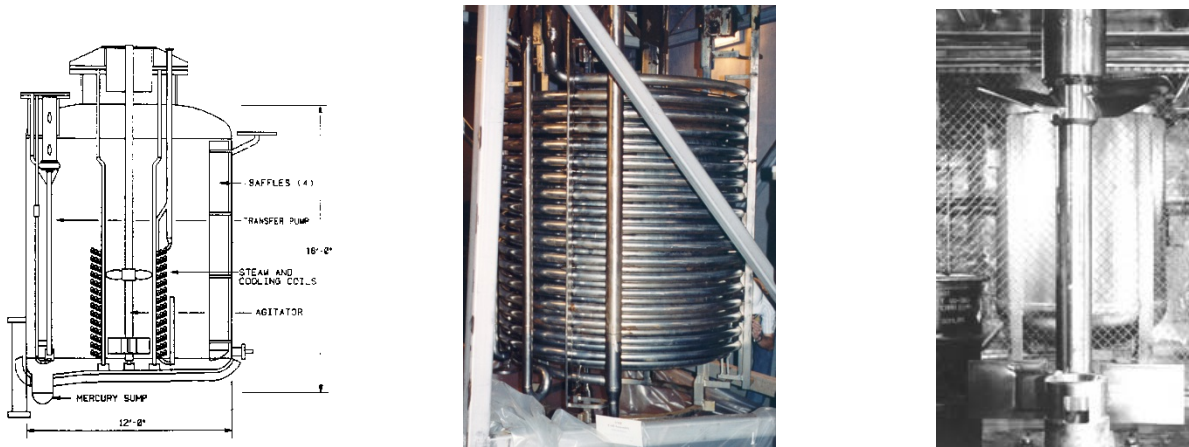


Figure 4. Schematic of SME vessel and photographs of the coil and agitator assembly (modified agitator assembly with fully welded blades) [35].

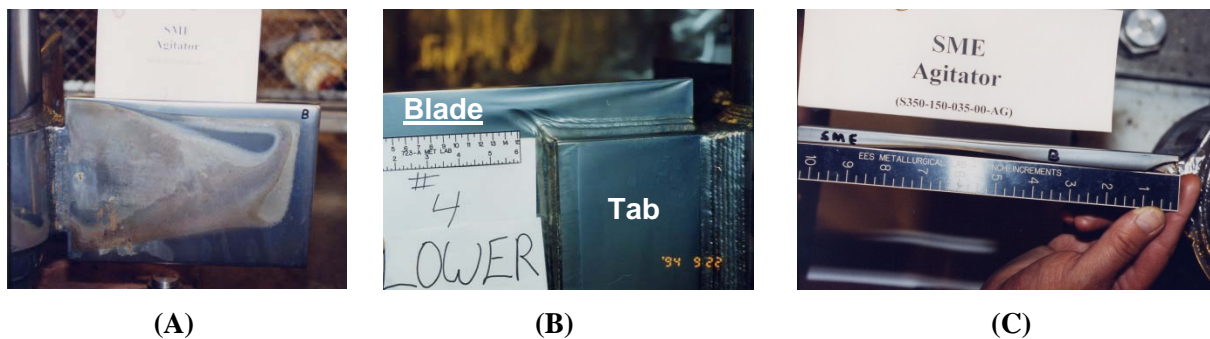


Figure 5. Lower agitator blade after cold nonradioactive operations. A) Front face only exhibiting minor edge rounding, B) degradation observed on back side at step transition between the attachment tab and the blade, and C) significant thinning of back side as observed from above the blade [31].

DWPF decided to pursue a test program to evaluate more E/C resistant alloys because of these accelerated failures. E/C tests were performed in a small slurry pot using two slurries and four different alloys (AISI 304L stainless steel, C-276, Stellite 6B, and Haynes Ultimet®) [35]. The first test slurry contained borosilicate frit suspended in deionized water, while the second slurry, representative of the DWPF SME process chemistry, contained simulated sludge, formic acid, and borosilicate frit. Test results indicated there was a 2 to 6 times increase in the alloy degradation rates in the acidified slurry indicating that there was a significant E/C effect. As a result of this testing, Ultimet® was selected and approved for use in the DWPF. Upper and lower agitator blade assemblies were fabricated from Ultimet® and have been in service for over twelve years without a failure. Investment cast Ultimet® elbows and wrought cover plates have also been added to the coils, which has extended the life of the coil assembly.

The test protocol used for this program began initially with electrochemical and immersion tests to establish general corrosion rates in a prototypic environment (i.e., temperature, pH, and aggressive species). The goal was to model the blending phase of the SME process so all tests solutions were

agitated. This was followed by erosion and erosion/corrosion tests in the slurry pot in a benign environment and full simulant. This is the generic test protocol outlined in ASTM G119, Standard Guide for Testing Synergism Between Wear and Corrosion [25].

3.0 Corrosion, Erosion, and Erosion/Corrosion Testing for the WTP

3.1 Tests versus Literature Data

Alloy selection is critical to ensure a forty plus year service life for the WTP. As shown in the previous sections, there are numerous variables that can affect general corrosion, localized corrosion, and E/C rates. These rates are difficult to predict using available literature because this data would not represent all aspects of the process and process chemistry. What would appear to be a seemingly small change in chemistry, (e.g., addition of mercury), or processing parameters, (e.g., slight temperature difference), may have a catastrophic effect on material performance. Localized corrosion mechanisms, pitting, SCC, and IGSCC are even more difficult to predict unless data appropriately envelopes current processing conditions. Pourbaix diagrams provide, as written by Marcel Pourbaix, “a panoramic view of the chemical configurations of a system predicted on a thermodynamic basis” as applicable to the electrochemical behavior of a metallic phase immersed in an electrolyte [36]. Pourbaix (Eh/pH) diagrams are useful as a starting point to help focus the scope of corrosion analyses; however Pourbaix diagrams only provide information of thermodynamically stable species resulting from chemical reactions but do not account for reaction rates or kinetic effects [36]. Therefore, testing must be performed in addition to a Pourbaix diagram study.

Some of the synergistic E/C and localized corrosion mechanisms can exist in extremely isolated regions of the process system where flow fields are disrupted by design features or sediment buildup. Complex systems and process chemistries including upset or accident conditions, extended down time, and extreme localized conditions must be considered. It is doubtful that accurate service life predictions can be made for these scenarios using only available public domain literature, which does not represent the waste or process chemistries that will be handled in the WTP. Even designing tests that would simulate the expected WTP process conditions would challenge material scientists and engineers. However, tests that simulate all anticipated representative conditions must be performed in order to decrease the likelihood of a premature failure of WTP BC&HTR components.

3.2 WTP Reviews

Numerous reviews of the WTP MOC and design processes have been performed beginning back as far as 2001. These reviews were performed by the world’s foremost subject matter experts in materials and corrosion science. Consistent with the results of this review, the consensus of all the reviews was that the expected MOC behavior in WTP cannot be predicted solely from available literature and, therefore, testing to support the WTP MOC selection and validation is needed. The reviews were performed by the following:

- Erosion Workshop (2014)
- Independent Review Team (2012)
- Differing Professional Opinion Review Team (2012)
- Bechtel Engineering (2012)
- Defense Nuclear Facility Safety Board (DNFSB) (2012)
- Department of Energy – Office of River Protection (DOE-ORP) Surveillances (2011, 2012)
- Blue Ribbon Panels (2001, 2004, 2008)

A comprehensive summary of all the recommendations, as well as BNI's plan to address these recommendations, are summarized respectively in Section 1.3 and Appendix A of BNI's Erosion Corrosion Test Strategy report and their Action Plan for Resolution of Erosion and Corrosion design Issues [37, 38]. The following summarizes some of the key recommendations:

- Perform additional testing guided by statistical methods (i.e., triplicate tests).
- Use appropriate ASTM Test Methods.
- Evaluate synergistic effects of erosion and corrosion.
- Test all process chemistries/conditions including upset and off-normal. Ensure all expected waste tank feed chemistries are enveloped by these tests.
- Test all materials and material conditions, welds, as-received, ground surfaces, etc.
- Perform longer term immersion tests to evaluate localized forms of corrosion and compare these results to the electrochemical test results.
- Perform electrochemical tests to evaluate time-dependent electrochemical material responses.
- Perform SCC testing including crack growth rate, U-bend and slow strain rate (SSR) tests.
- Perform testing of sufficient durations to allow extrapolation to 40 years.
- Test using actual waste solutions to reduce uncertainties.
- Evaluate PJMs and various piping conditions with E/C tests.

3.3 Test Methodology

The following provides a logical test methodology that could be applied to the WTP or to any materials selection/validation program where corrosion, erosion and erosion/corrosion synergism are concerns. The type and number of tests are dictated by how well the actual process is defined and by the candidate materials (low alloy vs. high alloy). The critical part is to fully understand the process, system design (piping, vessel, valves, jumpers, etc.) and fabrication processes that may affect (or introduce) the various corrosion, erosion, or E/C mechanisms. WTP design features that must be fully evaluated include (but are not limited to) the Purex and Grayloc style jumpers, centrifugal pump impellers and cases, FEP axial flow propeller pumps and steam jet eductors.

A well-defined test plan is necessary to validate MOC and to provide assurance that the materials will perform adequately for their anticipated design life. The goal of the test plan is to verify WTP MOC and ultimately to determine allowances necessary to complete the equipment and piping design. The plan can also be used to identify problematic process environments that may need additional evaluation. Providing a clear, defensible test strategy would also address the key recommendations of the various review teams. The plan will address general and localized corrosion mechanisms resulting from solutions with complex chemistries containing aggressive anions and inhibitor species. In addition, it will address the synergistic effects of erosion and corrosion in a flowing multiphase solution. The methodology initiates with simple bench-top laboratory tests and culminates with a large-scale prototypic test that represents the actual system configuration. There are three phases including: 1) short-term laboratory screening tests that quickly provide general and localized corrosion data for specific chemistries, 2) longer-term laboratory tests that are used to confirm results of the short-term tests and evaluate time-sensitive corrosion mechanisms, and 3) a full-scale, extended duration test that includes critical design elements representative of the actual system. Most of the tests are addressed by National Standard test protocols (e.g., ASTM and ASME) but some specifically designed tests, which better replicate the WTP process or optimize test duration, may be required. The key to a successful test program is to understand the process solution chemistry, solids, and process parameters (e.g., batch or continuous processing, temperature, pH, and flow rate) in order to design a test that will adequately represent the actual system.

The first and most important step would be to assemble process parameters for the entire WTP. To fully define the test matrix, a similar set of parameters must be developed for anticipated upset or off-normal conditions. The WTP Process Corrosion Data Sheets (PCDS) contain most of this information; however, they should be reviewed and validated against the current baseline operating strategies before beginning testing. Testing should include WTP MOC and alternate materials for areas where there is the potential for issues to arise with current MOC. Coupons used should include welded and wrought conditions representative of those used in the actual system. Testing should include pertinent waste species to ensure synergistic effects are addressed.

Figure 6 provides an outline of the test methodology. Initial screening tests can be performed using electrochemical test methods. These accelerated corrosion tests provide invaluable insight into material performance. Electrochemical tests provide corrosion data concerning general, pitting, crevice, and SCC mechanisms. Longer-term coupon immersion tests should also be performed in static and dynamic conditions to validate results from the electrochemical tests. Solution chemistry should be periodically monitored and replenished as necessary. Adequate exposure times are required to provide a reasonable assurance that localized corrosion mechanisms are not likely to initiate.

If SCC is suspected, additional testing may be required. Stressed U-bend coupons are normally incorporated into the long-term immersion test phase to evaluate the susceptibility of a material to SCC. In conjunction with the U-bend tests, SSR or K_{ISCC} tests should be performed. The SSR (notched specimens) is an increasing stress intensity test that provides the information on SCC susceptibility in a particular environment. K_{ISCC} tests with a ripple or step load coupled with high resolution crack monitoring equipment can provide a sensitive measure of crack growth that may provide material property data (threshold stress intensity) that can be used by system designers. Both SSR and K_{ISCC} are accelerated tests and each has limitations with exposure time and stress state that may make correlation to actual system components difficult. The important point is to avoid crack initiation all together. This can be accomplished by evaluating results of the electrochemical tests (passive film stability and evidence of localized corrosion mechanisms) and results from SCC and/or K_{ISCC} tests. This data would be used to modify system process parameters (i.e., chemistry and temperature) and component stress levels to avoid initiation of SCC in the WTP system.

There are numerous laboratory tests that have been developed to evaluate synergistic effects of erosion and corrosion. Some are addressed in National Standards while others are not. Selection of the appropriate test method should be influenced by how well the test models the actual system environment and its reproducibility, rather than by whether it is covered by a National Standard. Some E/C tests include, rotating cylindrical electrode, Miller/Slurry Abrasion Response (ASTM G-75), impingement test and Coriolis method. Each test has strengths and can be used for short-term E/C evaluations. Alternate E/C test methods are described by Roberge [29]. Only after all the short-term tests and the longer-term confirmatory tests have been completed and the data analyzed should a full-scale test such as a flow loop begin.

Methodology to Establish Design Basis for WTP Materials of Construction

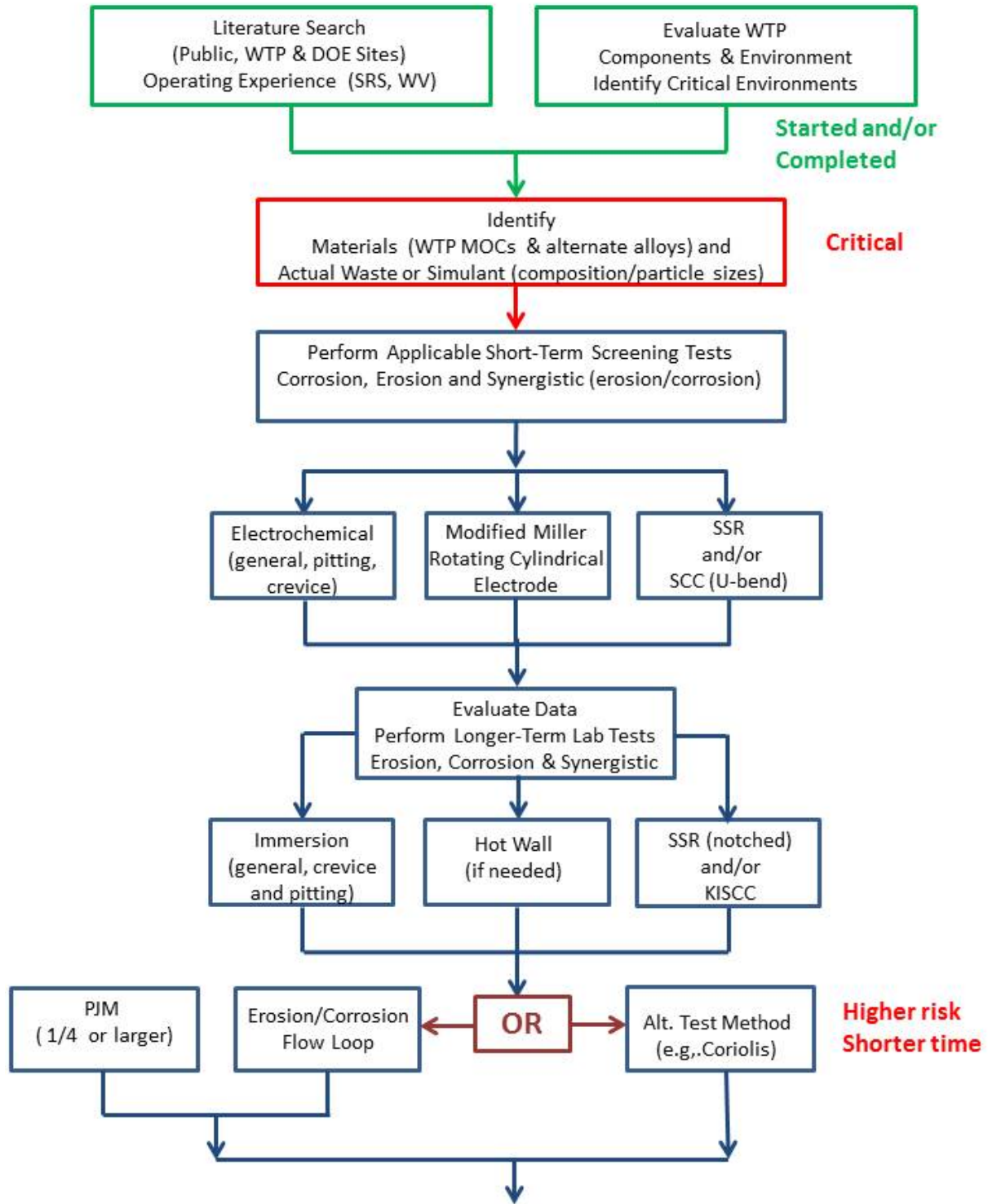


Figure 6. Test methodology for WTP MOC (continued on next page).

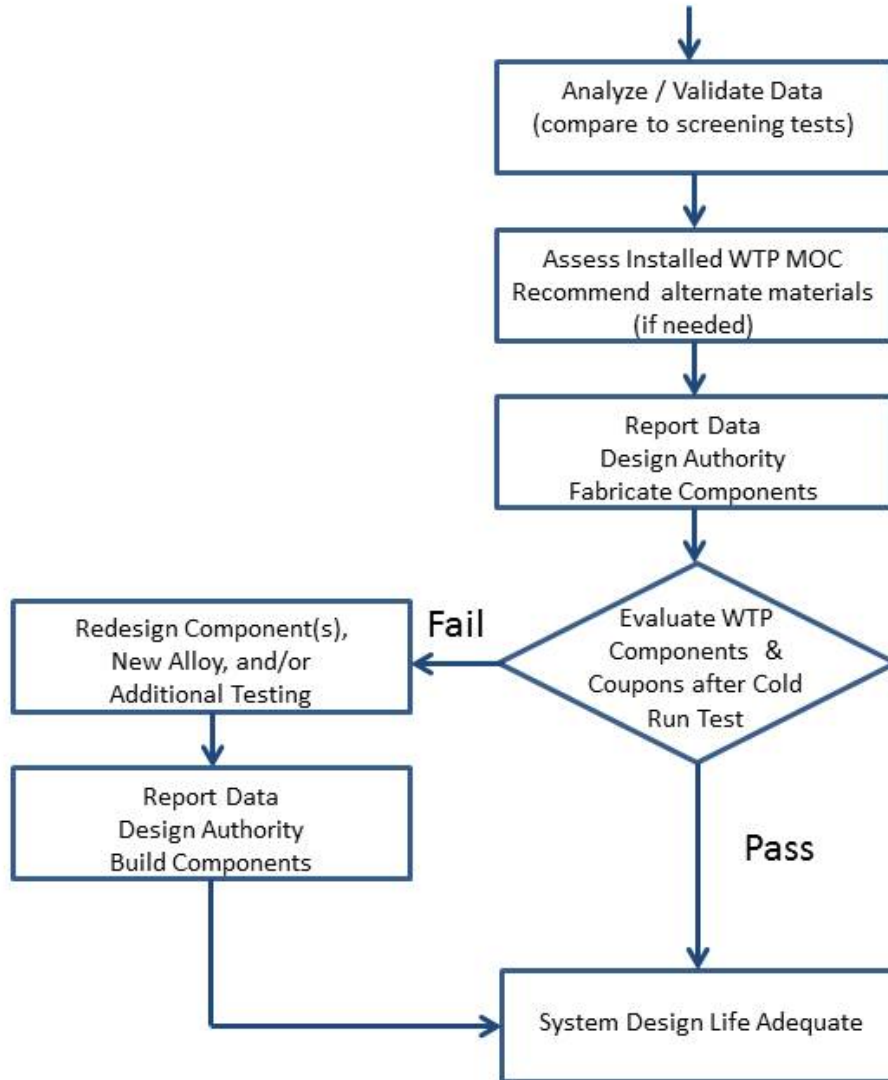


Figure 6 (continued). Test methodology for WTP MOC (continued from previous page).

4.0 Summary

Corrosion is an extremely complex process that is affected by numerous factors. Addition of a flowing multi-phase solution further complicates the analysis. The synergistic effects of the corrosive species as well as the flow-induced (Erosion/Corrosion) effects must be thoroughly evaluated in order to predict material degradation responses. Public domain data can help guide the analysis, but cannot completely solve the problem especially when the process is one-of-a-kind, designed for 40 plus years of service, and has no viable means for repair or replacement. This philosophy was exemplified by the DWPF and only after 15 plus years of successful operation has it been validated. There have been some “hiccups” some identified during the cold commissioning phase and some during radioactive operations, but they were minor and overcome. In addition, the DWPF system is flexible enough to tolerate most flowsheet changes and the design allows minor modifications and replacements – approaches not available with the WTP “Black Cell” design methodology.

Testing should not only be used for MOC selection but should also be used to develop the envelope that clearly defines the safe operating process conditions. With this data and a good working knowledge of the plant systems and local process conditions (solution chemistry/properties, and environmental conditions) plant operators will understand the physical limits of the WTP, which include normal and upset conditions as well as potential future process changes.

Based on the available data, the synergistic effect between erosion and corrosion is a credible – virtually certain – degradation mechanism and must be considered for the design of the WTP process systems. However, testing is recommended due to the number of variables (e.g., material properties, process parameters, and component design) that can affect synergy between erosion and corrosion and because the available literature is of limited applicability for the complex process chemistries anticipated in the WTP. Applicable testing will provide a reasonable and defensible path forward for design of the WTP Black Cell and Hard to Reach process equipment. These conclusions are consistent with findings from the various Bechtel, Independent Review Teams, and DOE reviews.

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